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Steam reforming of hot gas from gasified wood types and miscanthus biomass

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ABSTRACT

The reforming of hot gas generated from biomass gasification and high temperature gas filtration was studied in order to reach the goal of the CHRISGAS project: a 60% of synthesis gas (as $x(\text{H}_2) + x(\text{CO})$ on a N₂ and dry basis) in the exit gas, which can be converted either into H₂ or fuels. A Ni-MgAl₂O₄ commercial-like catalyst was tested downstream the gasification of clean wood made of saw dust, waste wood and miscanthus as herbaceous biomass. The effect of the temperature and contact time on the hydrocarbon conversion as well as the characterization of the used catalysts was studied. Low (<600 °C), medium (750 °C–900 °C) and high temperature (900 °C–1050 °C) tests were carried out in order to study, respectively, the tar cracking, the lowest operating reformer temperature for clean biomass, the methane conversion achievable as function of the temperature and the catalyst deactivation. The results demonstrate the possibility to produce an enriched syngas by the upgrading of the gasification stream of woody biomass with low sulphur content. However, for miscanthus the development of catalysts with an enhanced resistance to sulphur poison will be the key point in the process development.

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1. Introduction

Advanced biomass conversion technology will play a crucial role in reducing the need for oil and natural gas and the negative effects of greenhouse gases generated from fossil fuels [1–3]. Biomass and residues can be converted by thermal gasification into a gas mixture containing CH₄ and other hydrocarbons, CO, CO₂, H₂, tars and ash (SiO₂, MgO, CaO, K₂O, Na₂O, P₂O₅, etc) [4,5]. This mixture after several treatments can be transformed into H₂ and/or liquid fuels, Biomass to Liquids (BTL). Recent reports have stated that the 15% of the transportation fuels required in 2030 can be produced by the 25% of the agro-forest residues produced world wide and transformed by gasification into BTL or Bio-SNG respectively [6]. The possibility to increase the overall yield of such a process, as

proposed in the CHRISGAS Project, is related to the hot gas cleaning followed by the catalytic hydrocarbon conversion to enrich in H₂ and CO the gas produced by gasification. The CHRISGAS Project is based on the Värnamo Biomass Gasification Centre (VBGCC) in Sweden, a unique 18 MW(thermal input) pressurised circulating fluidized bed (CFB) system [7]. The plant modification, according to the project, will concern of an additional unit of hot gas filtration and a reforming unit, designed on the bases of the experience and knowledge acquired in the project [8]. The tests reported here are related to a 100 kW thermal input CFB gasifier located at the Delft University of Technology. One of the goals of the project was to reach a 60% of synthesis gas ($x(\text{H}_2) + x(\text{CO})$ on dry and free nitrogen basis) in the exit gas, which can be further converted either to H₂ or liquid fuel, the latter with an efficiency related to

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the LHV of the gas exit from the reforming of 55%, 60%. Within CHRISGAS, the combination of hot gas filtration and upgrading of the gases is on the basis of high efficiency and this has been studied in pilot plants using a commercial-like catalyst comparing catalytic activity measured by methane conversion at different temperature and deactivation features.

In order to convert the hydrocarbons present in the gasification stream, steam or autothermal reforming, as well as partial oxidation processes can be used [9]. The two possibilities foreseen in the project were: 1) the thermal partial oxidation at 1300 °C with a calculated loss of 23% of the LHV with respect to the entrance gases; and 2) the autothermal reforming at 1000 °C (outlet temperature) with a 15% loss of LHV with respect of the inlet gas but requiring 30% less oxygen than the thermal partial oxidation. The calculation is based on a filter temperature of 800 °C and a final syngas concentration at the equilibrium (70% on dry and nitrogen free based).

Although the above are well-known processes for the production of H₂ and syngas [10], their feasibility applied to a gasification generated gas depends on the activity and stability of the catalysts. The main problem of the reforming process after hot gas filtration is related to the deactivation, especially due to the sulphur poisoning, with additional long term effect on Ni sintering of the alkali, passing throughout the hot gas filter [11]. In the previous work, the effects of these contaminants in the deactivation and catalytic performances have been studied under laboratory conditions by exposure of the catalyst to a simulated atmosphere [12]. In this work, since the deactivation effects are biomass dependent, they were studied in a reactor directly connected after a CFB gasifier in which different feedstock have been fed. The present research illustrates the steam reforming tests on a Ni based commercial-like catalyst carried out after a 100 kW thermal input CFB gasifier and a hot gas filter fed with three types of biomass and specifically clean saw dust, waste wood and miscanthus at different temperature and residence time to identify the reaction pathway and the catalyst activity and deactivation. The catalyst used in the tests have been characterised to describe its modification during time on stream and to make the presence of poisoning species.

2. Material and methods

2.1. Catalytic tests

The tests were carried out in a pilot plant at the Process and Energy Department at the Delft University of Technology

equipped with a 100 kW thermal input steam/oxygen CFB gasifier and a hot gas filtration system [13]. A slipstream from the product gas after the hot filter was fed to a bench scale reformer. During the first set of the reforming experiments (low temperature) the filter worked at 600 °C and the pipeline connecting it to the reformer was kept at ca. 350 °C in order to avoid tar condensation, whereas in the second set of experiments (middle and high temperature), the filter worked at 800 °C and the temperature was close to that of the filter. The reformer reactor is made of an INCOLOY 800 HT tube 90 cm long with an internal diameter of 4 cm and an external diameter of 5.2 cm. The gas flow (from 10 dm³ min⁻¹ to 20 dm³ min⁻¹) from the gasifier was drained by a downstream diaphragm vacuum pump (KNF Neuberger) and was measured by a rotameter. The temperature inside the reactor is measured with a sliding thermocouple placed in the catalytic bed, thus making it possible to measure the axial temperature before (inlet temperature) and after the catalyst (outlet temperature). The reactor could work in reforming mode heated by means of an oven reaching 1100 °C (T_{out} till 1050 °C) or by using oxygen to achieve autothermal process conditions. The gas composition was analyzed after gasification downstream the filter (i.e. before the reforming) and after the reforming. The tar analysis was carried out with a gas chromatography-flame ionization detector (GC-FID) analysis; the gas was analyzed by micro GC connected on line with the gas stream expressed as volume volume⁻¹, and the results represent the average of at least 5 analysis with the Σx(i)% of the gas species between 98% and 102% [13].

A Ni-MgAl₂O₄ commercial-like catalyst [12] was tested, using the gasification gas from three lignocellulosic biomass types: a clean wood made of saw dust (Wood A), a waste wood (Wood B), and miscanthus as herbaceous type biomass. Sand and olivine were used as bed material in the gasifier using each of the three types of biomass; moreover, during the tests carried out with miscanthus, Fe containing magnesite was also used to avoid agglomeration due to the reaction of the alkali present in the biomass with the silica present in sand and olivine. The effect of the outlet temperature and the contact time on the hydrocarbon conversion was studied. A summary of the reforming tests performed is displayed in Table 1. The middle and high temperature tests were carried out at lower residence time to discriminate among the different biomass; comparison is shown only with tests carried out under similar conditions.

2.2. Characterization techniques

Powder X-Ray Diffraction (PXRD) analyses were carried out using a Philips PW1050/81 diffractometer equipped with

Table 1 – Summary of the reforming tests carried out downstream the gasifier.

Test	Low Temperature (<600 °C)	Middle Temperature (750 °C–900 °C)		High Temperature (940 °C–1050 °C)	
Fuel	Wood A, Wood B, Miscanthus	Wood A,	Wood A, Wood B	Wood B	Miscanthus
Loaded Catalyst (cm ³)	36	25	46	46	46
Gas Flow (cm ³ min ⁻¹)	2000	2000	8000	8000	8000
τ (s)	1.08	0.75	0.35	0.35	0.35

a graphite monochromator in the diffracted beam and controlled by a PW1710 unit (CuK α -Ni filtered, $\lambda = 0.15418$ nm). A 2θ range from 10° to 80° was investigated at a scanning speed of 70° h^{-1} . Average sizes of crystallites of the Ni⁰ phase were calculated in the (200) direction by using the Scherrer equation: $D = K\lambda/(\beta\cos\theta)$, where D is the average crystallite size, K is the shape factor for the average crystallite (the expected shape factor is 0.9), λ is the X-ray wavelength (0.154056 nm for Cu K α_1), θ is the Bragg angle, and β is the full width at half-maximum (FWHM) in radians [$\beta = (B^2 - b^2)^{1/2}$, where B is the measured FWHM and b is the instrumental broadening, which was determined by collecting the diffraction pattern of a silicon line-width standard]. Temperature Programmed Oxidation (TPO) analyses were carried out with an O₂/He 5/95 v/v respectively (total flow rate 20 cm³/min) gas mixture in the 100°C–950 °C temperature range in a Thermo-Quest CE instruments TPDRO 1100. A Boc Edwards EXC 120 Mass Spectrometer was used to analyze the gas coming out from the TPDRO 1100. CHNSO analyses data were obtained by means of CE Instruments EA 1110. Specific surface area BET (Brunauer, Emmet and Teller) measurements were carried out in a Micromeritics ASAP 2020 instrument by N₂ adsorption/desorption at -196°C . Samples were previously degassed under vacuum and heated up to 250 °C maintained for 30 min. SEM/EDS analyses were performed by using an EVO 50 Series Instrument (LEO ZEISS) equipped with an INCAEnergy 350 EDS micro-analysis system and an INCASmartMap for imaging the spatial variation of elements in a sample (Oxford Instruments Analytical). The accelerating voltage was 25 kV, the beam current 0.15 nA, and the spectra collection time 100 s.

3. Results and discussions

3.1. Catalytic tests

The content in ash and sulphur is biomass dependent, the general trend for the biomass here used is Wood A < Wood B < Miscanthus. In this work, in order to evaluate the catalytic activity, the reforming of the biomass generated gas was carried out under three different conditions: at low temperature (<600 °C) having as main purpose the tar cracking; at middle temperature (750°C–900 °C) with woody biomass to

determine the low temperature limit at which the reformer can be carried out with biomass containing less sulphur; and at high temperature (940°C–1050 °C), which are the industrial-like conditions, and are useful to establish the conversion limit and evaluate the deactivation of the catalyst by thermal sintering, sulphur poisoning and carbon deposition. The volume fraction of water in the inlet stream during the tests was ca. 50%–60%, therefore the catalysts in the reforming reaction worked at high steam to carbon ratio.

The benzene + toluene conversion and the methane conversions at low temperature are shown in Fig. 1. The tests with wood B showed the highest amount of C6–C7 at the inlet of the reforming (Table 2). The C6–C7 conversion decreased as the sulphur content in the biomass was higher, but increased at higher temperature. The negative methane conversion values obtained when the C6–C7 conversion was high (tests with Wood A and Wood B) could be related to the methane formation, mainly by toluene hydrocracking and to a lesser extent from benzene hydrocracking, coupled with the low methane conversion. However, the positive value of the methane conversion achieved during the tests with miscanthus may be attributed to the fact that C6–C7 cracking and hydrocracking could be more affected than the methane reforming by a high coverage of the surface by sulphur species (sulphur adsorption) since the C6–C7 reaction requires an higher number of vicinal catalytical sites than that of methane reforming. The synthesis gas ($x(\text{H}_2) + x(\text{CO})$) on dry and nitrogen basis) before and after the reformer is compared in Fig. 1. A decrease in the synthesis gas ($\text{H}_2 + \text{CO}$) content and an increase of H_2 was observed due to the combination of the hydrogen consumption in the hydrocracking reaction and the hydrogen production from CO and H₂O due to the water gas shift (WGS) reaction. The undesired methanation and Boudart reactions could also take place at the used temperatures modifying the H₂ and CO content.

The results obtained during the reforming between 750 °C and 900 °C of the gas produced by Wood A gasification are shown in Fig. 2. During the tests at $\tau = 0.35$ s, an increase in the converted methane was observed as the temperature increased in agreement with the thermodynamics of the endothermic reforming reaction. At 900 °C the content of methane in the reformed gas was ca. 2%. The same trend was observed in the synthesis gas composition ($x(\text{H}_2) + x(\text{CO})$). On the other hand, in the tests at $\tau = 0.75$ s, high methane

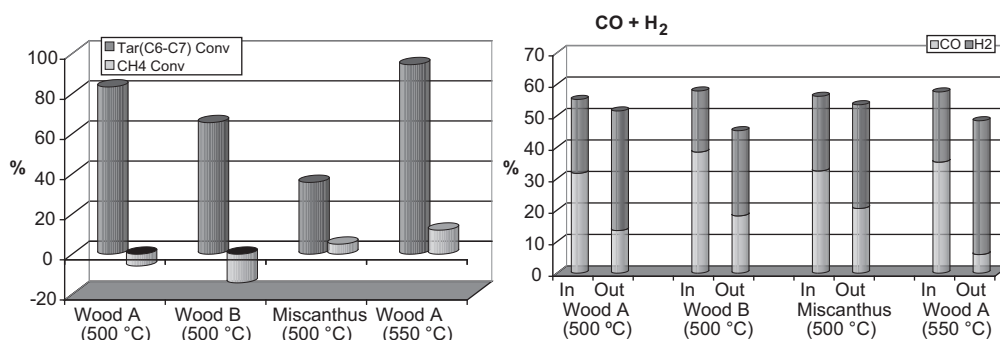


Fig. 1 – Methane, C6+C7 (benzene + toluene) conversions (as % of volume volume⁻¹) and synthesis gas (as $x(\text{H}_2) + x(\text{CO})$) obtained during the reforming of the biomass generated gas at low temperature.

Table 2 – Composition (on dry bases) of gases before and after the catalytic reactor ($\tau = 1$ s) in the low temperature tests carried out after gasification of different biomass.

Biomass	WOOD A		WOOD B		MISCANTHUS		WOOD A	
	Before SR	After SR	Before SR	After SR	Before SR	After SR	Before SR	After SR
Tout (°C)	500 °C		500 °C		500 °C		550 °C	
CO ₂ (%)	29.9	35.1	27.6	37.7	29.1	31.8	27.89	38.05
CO (%)	26.6	11.9	33.7	15.8	28.0	17.6	30.30	5.15
H ₂ (%)	19.7	33.4	17.0	23.6	20.5	28.2	19.17	37.08
N ₂ (%)	16.0	12.1	12.4	13.0	13.6	14.3	14.06	12.76
CH ₄ (%)	7.0	7.4	8.9	9.6	8.0	7.6	7.86	6.92
Benzene (%)	0.60	0.10	0.79	0.28	0.67	0.39	0.59	0.03
Toluene (%)	0.13	0.02	0.16	0.05	0.12	0.08	0.14	0.01

conversion ($x(\text{CH}_4)$ decreased from 6.3% to 0.8%) and synthesis gas content ($x(\text{H}_2) + x(\text{CO})$ on a N₂ and dry basis) $\geq 60\%$) were achieved indicating a good activity of the catalyst with a low sulphur containing gas ($x(\text{H}_2\text{S})$ from 10 cm³ m⁻³ to 30 cm³ m⁻³). The higher increase of the H₂ with respect to the CO was related to the combination of the contribution of the reforming and the WGS reaction. Although the tests using biomass can be affected by a change in their composition, the differences here observed were mainly related to the contact time. These results indicated that a temperature close to that of the hot gas filter could be sufficient to obtain high syngas yield and high efficiency, leading, also to conclude that these conditions are compatible with a steam reforming process.

The reforming tests of the wood B gasification stream were performed up to high temperature to achieve high conversion, Fig. 3. A general increase of methane conversion with increasing temperature and decreasing contact time was observed. It should be reminded that the sulphur content in this biomass is larger than in wood A, and that the equilibrium of the reaction of sulphur deactivation of the nickel catalyst by dissociative chemisorption of H₂S on the metallic surface (1) [14] is not only dependent on the partial pressure of hydrogen ($P(\text{H}_2\text{S})P(\text{H}_2)^{-1}$) and water but is also affected by the increase of the temperature which shifts the equilibrium towards the reactant [15,16].



At 975 °C the methane concentration was below 1% at the exit of the reforming reactor. Under these conditions, the synthesis gas ($x(\text{H}_2) + x(\text{CO})$ on a N₂ and dry basis) is ca. 70%. The tests carried out increasing the contact time suggest

a further increase of conversion can be obtained by the optimisation of this parameter as reported in the tests using Wood A. The differences were not as remarkable as in the tests with Wood A, probably because of the extent of polluted sites which decrease the reaction rate.

Finally the data obtained during the reforming of the miscanthus generated gas using both olivine and magnesite as bed materials are summarized in Fig. 4. Miscanthus further increased the sulphur level by a factor of > 2 (i.e. $\text{H}_2\text{S} > 200 \text{ cm}^3 \text{ m}^{-3}$). The increase of sulphur increased NiS formation and decreased catalyst activity. Likewise during the tests with wood B, the methane conversion increased with temperature. However, when using olivine as bed material, a methane conversion and a synthesis gas concentration of 63% were achieved. This value is significantly lower than that obtained with the Wood B. Conversely, better results were obtained by using magnesite as bed material, giving a methane concentration below 0.5% in the outlet gas. As previously reported [13], magnesite, having iron as a minor component (the mass fraction of Fe₂O₃ is 3.36%) modifies the composition of the gasification stream; it increases the hydrogen content (50% on a dry base) and reduces the amount of hydrocarbons and CO. The lower amount of methane and the increase in H₂ content in the gas, shift the equilibrium of reaction (1) towards the reactants avoiding the formation of NiS and the deactivation of the catalyst, improving the performances of the catalyst during the tests.

Calculation on the energy balance of the reactor shows that a 4% of methane conversion by reforming induces a 100 °C decrease due to the endothermic character of the reaction. Therefore, an autothermal process needs to be carried out with

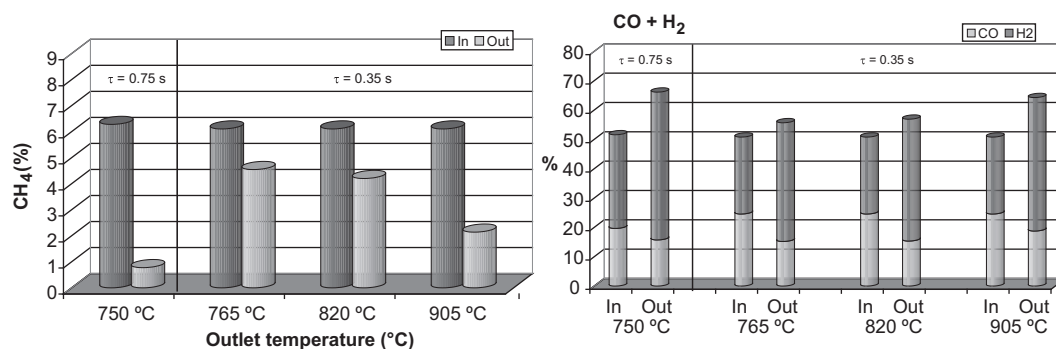


Fig. 2 – Methane and synthesis gas composition (as $x(\text{H}_2) + x(\text{CO})$) before and after the reforming of a Wood A generated gas. Influence of the contact time and temperature.

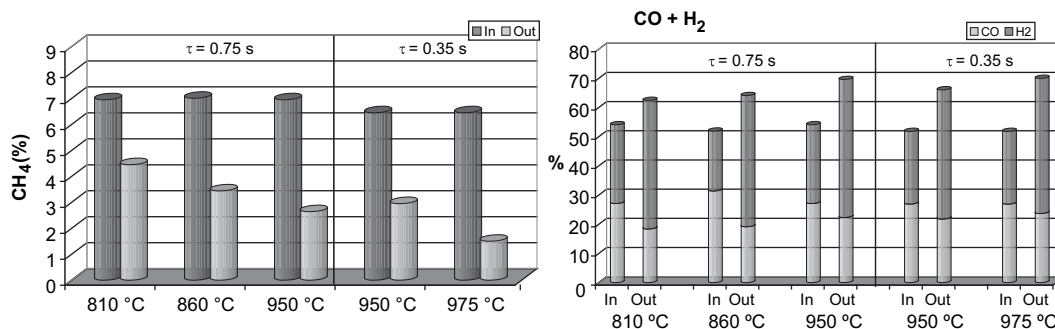


Fig. 3 – Methane and synthesis gas composition (as $x(\text{H}_2)\%$ + $x(\text{CO})\%$) during the reforming of a Wood B generated gas. Influence of the contact time (compared at 950 °C) and temperature (at contact time 0.75 and 0.35 s).

an inlet temperature in the catalytic bed of about 1150 °C. This consideration has two opposite effects: on one hand, the conversion can be higher due to the higher temperature having a positive effect on the thermodynamic equilibrium; on the other hand, the high temperature can lead to the sintering of the Ni. In fact, even if these conditions are not far from an industrial ATR, the atmosphere in which the process is carried out differs due to the presence of alkali, which decreases the melting point of the Ni particles, and to the presence of sulphur forming NiS characterised by an high tendency to sintering.

3.2. Characterization of the used samples

The fresh catalyst was formed by nickel oxide, a spinel-type phase and a small amounts of $\alpha\text{-Al}_2\text{O}_3$. No activation procedure is required; the catalyst could be activated during time on stream because of the reducing power of the gasification stream whenever the temperature is above 500 °C. After the catalytic tests, the catalyst was reduced with the exception of the catalyst tested with gasified Wood B at 500 °C, where a small amount of NiO was observed. The catalysts tested with miscanthus shows the presence of a side phase of SiC. The presence of crystalline carbon (graphite), bulk NiS or other inorganic species (ash) was not observed in the diffraction patterns. The source of Si cannot be determined since it is present in biomass, bed material (olivine) and filter. In order to study the sintering of the metallic particles Ni⁰ crystallite sizes were obtained by the Scherrer equation for the spent samples (Table 3). For comparison purposes, the fresh catalyst was reduced in the laboratory under standard conditions. The

values depended not only on the biomass feed stock but also on the reaction temperature as well as on the inlet gas composition affected by the bed material in the gasifier. Ni⁰ crystallite sizes were smaller for the catalysts tested at low temperature, even smaller than that obtained for the reduced catalyst. This feature could be explained taking into account the lower operating temperature (500 °C for the tests and 750 °C for the reduced sample). Moreover the small value obtained for the catalyst tested with the gas coming from the gasification of Wood B was related to the not complete reduction of Ni present also as NiO phase in the XRD. The sintering of the active phase occurred during the tests at high temperature, the largest crystallite size value was obtained with the catalyst tested with miscanthus and using olivine as bed material in agreement with the high temperature required to increase the low catalytic activity. This phenomenon could be related not only to the thermal sintering but also to the sintering promoted by the sulphur, which could increase the nickel mobility [17] leading to the formation of larger metallic particles [18]. Conversely, the catalyst tested in the reforming of the gas coming from the gasification of miscanthus using magnesite as bed material did not greatly sinter, the presence of a larger amount of H₂ in the gasification stream could avoid the formation of NiS as the above proposed, decreasing the sintering process as well. More characterization is required for supporting this information, being work still in progress.

Specific surface area and pore volume values of the fresh, reduced and used samples are summarized in Table 3. The decrease of the surface and pore volume values were temperature dependent: the higher the operating

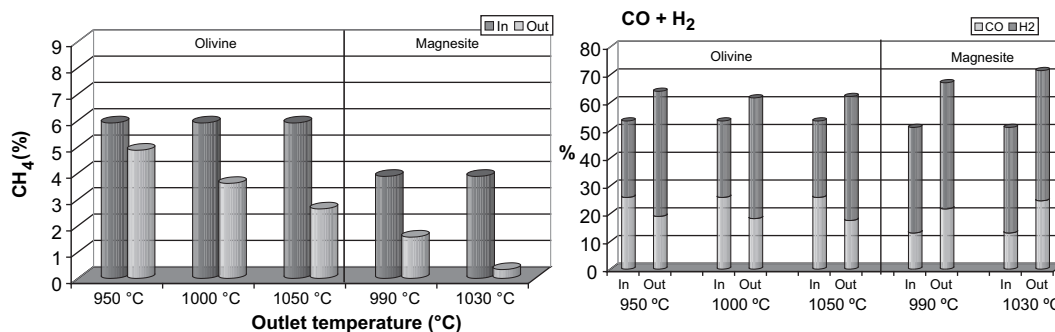


Fig. 4 – Methane and synthesis gas composition (as $x(\text{H}_2)\%$ + $x(\text{CO})\%$) during the reforming of Miscanthus generated gas (residence time 0,35 s). Influence of the temperature using olivine and MgO as bed materials.

Table 3 – Ni crystallite size, specific surface area and pore volumes of the fresh, reduced and used catalysts.

Sample	Ni ⁰ crystallite size (nm)	S _{BET} (m ² g ^{−1})	V _p (cm ³ g ^{−1})
Fresh	–	10.6	0.11
Reduced ^a	21	12.8	0.11
Wood A (used at T of 500 °C)	18	7.4	0.11
Wood B (used at T of 500 °C)	12	9.2	0.14
Miscanthus (used at T of 500 °C)	19	9.9	0.11
Wood A (used at T of 750 °C)	26	7.2	0.09
Wood B (used at T < 1050 °C)	56	6.0	0.06
Miscanthus MgO (used at T < 1050 °C)	50	5.8	0.06
Miscanthus Olivine (used at T ≤ 1050 °C)	73	6.2	0.07

a H₂/N₂ gas mixture at 750 °C.

temperature, the lower the measured values, confirming the thermal sintering of the catalysts support, which could also promote the sintering of the Ni⁰ particles. However, the deposition of particles on the surface of the catalyst (see SEM characterization below) and the pore blockage by large Ni⁰ particles could also contribute to the decrease of the surface area and pore volume. The high pore volume value of the catalyst used during the reforming of the Wood B gasification stream at 500 °C could be attributed to the formation of amorphous carbon in macropores (not detected using N₂ adsorption and desorption). However, it should be remarked that the surface area showed a certain degree of stability indicating that the sintering effect on the surface area of the support is not important after 30 h of time-on-stream. The characterization results obtained here are in line with those previously obtained in the deactivation of similar catalysts under simulated conditions [12].

TPO/MS of the catalysts tested at low temperature with the different biomass were performed to study the effect of the biomass in the carbon formation during the reforming. The oxygen consumption due to NiO and/or the carbon oxidation was observed together with the evolution of CO₂ due to carbon oxidation (Fig. 5). Only a small amount of CO is evolved, indicating that most of the carbon was removed as CO₂, thus it was not plotted in Fig. 5. The oxidation of Ni⁰ took place between 350 and 400 °C, while the temperature of carbon removal by

oxidation was related to the type and the stability of carbon. In Wood A, the first O₂ consumption was related to the oxidation of Ni⁰ to NiO. The carbon formed during the tests is removed at ca. 650 °C indicating whiskers formation or graphite; the latter, however, were not observed by PXRD. Concerning the catalyst tested with the gas obtained by Wood B gasification a larger amount of carbon was observed, in agreement with the larger pore volume values obtained, but it was removed at lower temperatures. Conversely, the reforming of the miscanthus generated gas gave rise to two different types of carbon, removed at low and high temperature. The mass fraction of carbon obtained by CHNS analyses was 0.46%, 1.62% and 0.53% for Wood A, Wood B and Miscanthus respectively. These results are in agreement with those obtained by TPO analysis. The results could be explained when taking into account that the formation of NiS could decrease the formation of carbon [19]; moreover the high ash content present in the miscanthus could facilitate the carbon removal.

SEM/EDS analyses of the used samples were performed in order to investigate the morphology and composition of the spent samples. The used catalysts were formed by Ni metallic particles supported on the support (spinel phase); moreover some particles and some carbon whiskers were observed on the surface of the catalysts. EDS analyses showed that the particles on the surface of the support were constituted by Si, Fe, alkali (Ca, K, Na). The presence of alkali in the surface of the catalyst may also have led to pore blockage by crystallization inside them [12]. The presence of Si, Fe or alkali (Ca, K, Na) indicates two different sources of poisoning possibilities: fine ash passing through the filter and bed materials such as magnesite and olivine containing Fe-MgO or Fe-Silicates, sources probably responsible also for the SiC evidence in the XRD.

3.3. Conclusions

The use of clean wood (saw dust) leads to high tar conversion already at low temperature (550 °C) and high methane conversion at 750 °C. On the other hand, the use of woody waste with a higher sulphur content ($x(\text{H}_2\text{S}) \approx 100 \times 10^6$ in the inlet gas) required higher temperature to reach a similar conversion. Nevertheless an enriched synthesis gas production ($x(\text{H}_2) + x(\text{CO}) > 70\%$ on dry and N₂ free bases) was produced at moderate temperature (975 °C–1000 °C) demonstrating the possibility to run the process with a large advantage in terms of efficiency and fuel production with respect to the thermal partial oxidation option. Finally, using

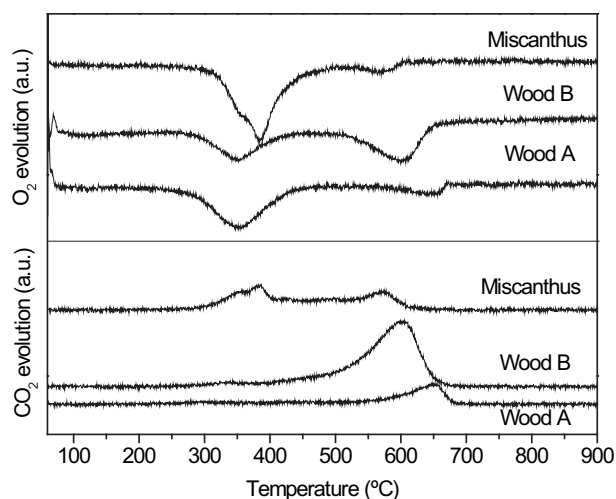


Fig. 5 – Evolution of O₂ and CO₂ gases during the TPO analysis of used catalysts.

miscanthus herbaceous biomass in the gasifier (*miscanthus*) a $x(\text{H}_2\text{S}) > 200 \times 10^6$ is present in the inlet gas to the reforming. In these conditions only ca. half of the methane was converted at 1050 °C (with a $x(\text{H}_2) + x(\text{CO}) = 63\%$). Therefore, using *miscanthus*, the advantage with respect to the thermal process is still present but needs to be evaluated in the long term taking into consideration the deactivation risk due to the presence of alkali and the formation of NiS which can induce Ni sintering.

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